Production of higher alcohols from CO and H2

Schumann, Max; Jensen, Anker Degn; Nielsen, Monia Runge; Hansen, Thomas Willum; Christensen, Jakob Munkholt

Publication date:
2018

Document Version
Publisher's PDF, also known as Version of record

DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

Production of higher alcohols from CO and H_2

Max Schumann[1], Anker Degn Jensen[1], Monia Runge Nielsen[2], Thomas Willum Hansen[2], Jakob Munkholt Christensen[1].

[1]Department of Chemical and Biochemical Engineering, [2]Center for Electron Nanoscopy, Danmarks Tekniske Universitet, Søltofts Plads, 2800 Lyngby, Denmark

Combined mechanistic and catalytic reactor studies were applied to gain mechanistic insights into the catalytic cycle of producing C_2-oxygenates (C_2-O) from CO and H_2 over supported single metallic Rh catalysts.

Background

Supported metallic Rh has been shown to form C_2-O with a wide range of selectivities and CO conversion levels [1,2]. The present study seeks to understand the origin of this wide spread and become able to make catalysts with high C_2-O selectivity at simultaneous high syngas conversion at an acceptable level of metal loading.

Catalytic performance during the CO-H_2 reaction for 1% Rh dispersed on SiO_2 or ZrO_2 – impact of CO/H_2 pressure

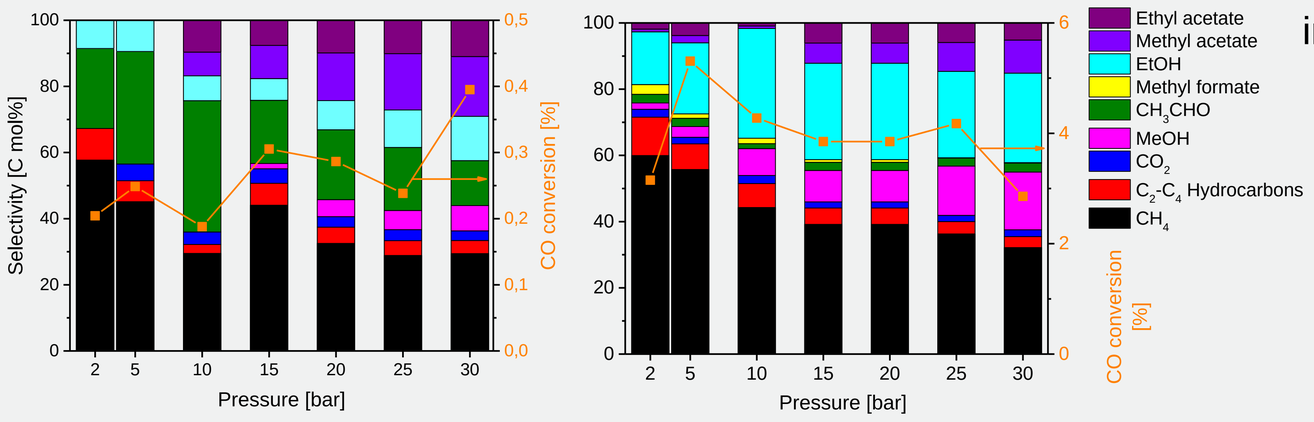

Figure 1: Product distribution and CO conversion as a function of the CO/H_2 gas feed pressure for the CO-H_2 reaction over 1% Rh/SiO_2 (left) and 1% Rh/ZrO_2 (right). Catalysts were prepared via wet impregnation of $Rh(NO_3)_3$ solution. m_{cat} = 2.00 g, flow = 37 SmL/min, $T_{Rh/SiO2}$ = 250 °C, $T_{Rh/ZrO2}$ = 225 °C.

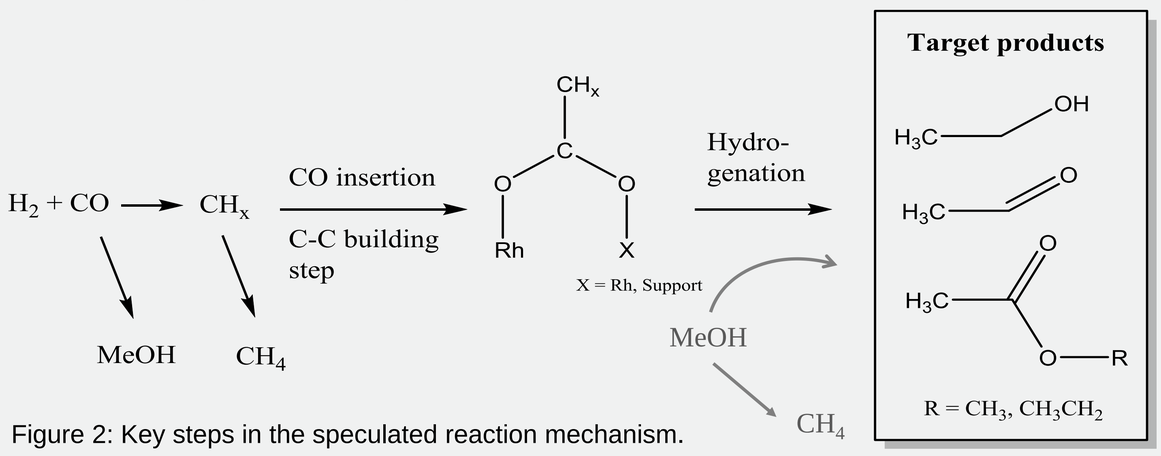

Figure 2: Key steps in the speculated reaction mechanism.

- Elevated CO/H_2 gas feed pressure is required to obtain C_2-oxygenates as majority product over Rh catalysts.
- The choice over the support has a strong impact on the CO conversion level (ca. tenfold increase for ZrO_2 compared to SiO_2-supported Rh).
- Further elevated CO/H_2 pressure conditons shifts the distribution within C_2-O products (AcH/EtOH/acetate esters).

Role of in situ formed MeOH as reactant

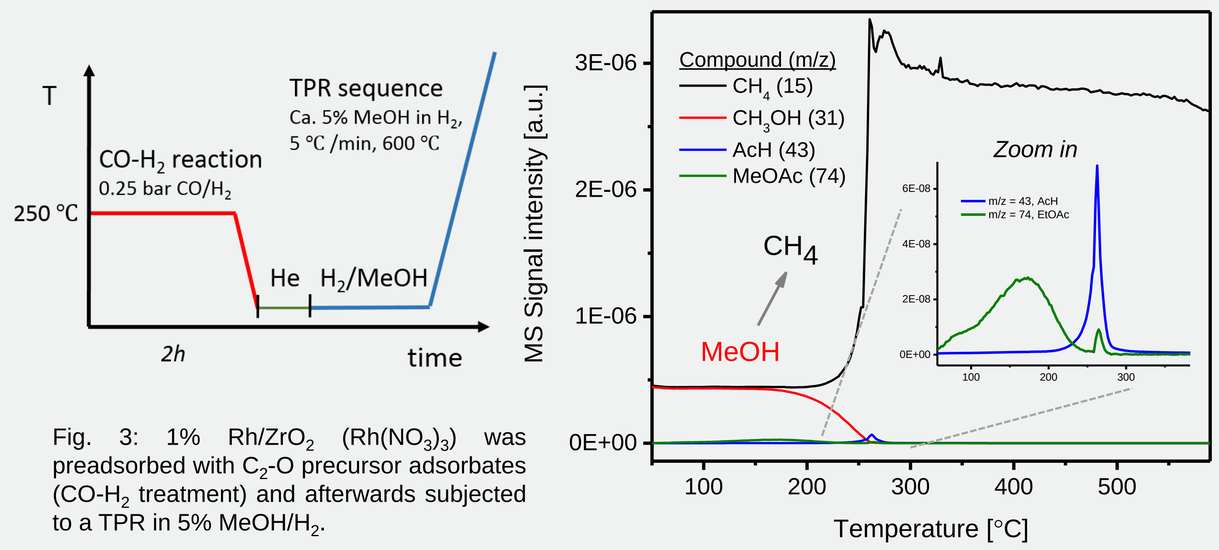

Fig. 3: 1% Rh/ZrO_2 ($Rh(NO_3)_3$) was preadsorbed with C_2-O precursor adsorbates (CO-H_2 treatment) and afterwards subjected to a TPR in 5% MeOH/H_2.

Significant levels of ester products were found at high CO/H_2 pressure conditions. It was shown, that surface C_2-O precursor adsorbates can react in a H_2/MeOH atmosphere to methyl acetate.

Topological changes to the Rh catalyst

$RhCl_3$-derived catalysts are reported to be better C_2-O producing catalysts. Remaining Cl is assumed to mobilize the Rh through involvement in formation of Rh-carbonyl complexes.

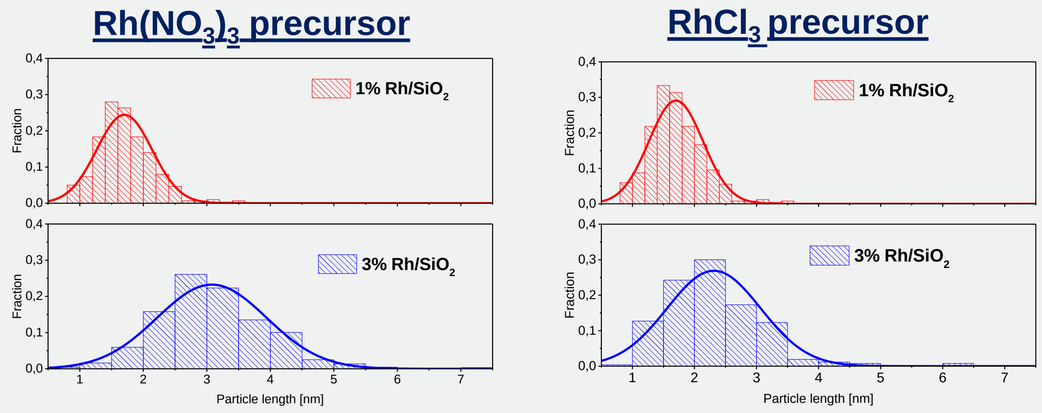

Figure 4: TEM derived particle size distribution analysis imaging for 1 and 3 wt% loaded Rh/SiO_2 catalysts from $Rh(NO_3)_3$ (left) and $RhCl_3$ (right) as precursor material.

- 50 bar CO-H_2 reaction treatment of 3% Rh/SiO_2 (from $RhCl_3$) resulted in a complete depletion of the Rh. Most likely due to volatility of formed carbonyls.

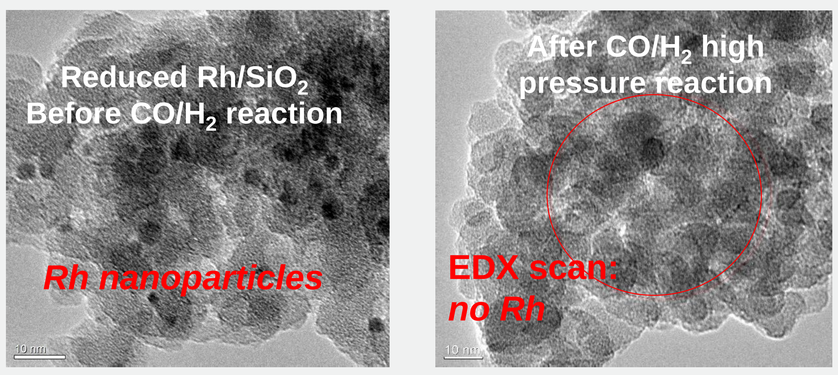

Figure 5: TEM images of 3% Rh/SiO_2 (from $RhCl_3$) before (left) and after (right) CO-H_2 reaction at 50 bar, 275 °C.

Outlook

- *In situ* EXAF: Rh/support exposed to different CO pressures.
- Environmental TEM – identifying possible topological changes of the Rh during the exposure to CO atmospheres.

References

[1] Ichikawa, J. Chem. Soc. Chem. Comm. **1978**, *13*, 566.
[2] Bhasin et al., J. Catal. **1978**, *54*, 120.

THE VELUX FOUNDATIONS
VILLUM FONDEN VELUX FONDEN